Synthesis, Functionalization and Characterization of Wood Pulp-Polyvinyl Alcohol Composites for Abatement of Toxic Metals from Water Bodies

A
SYNOPSIS
SUBMITTED FOR THE AWARD OF DEGREE OF
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IN
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BY

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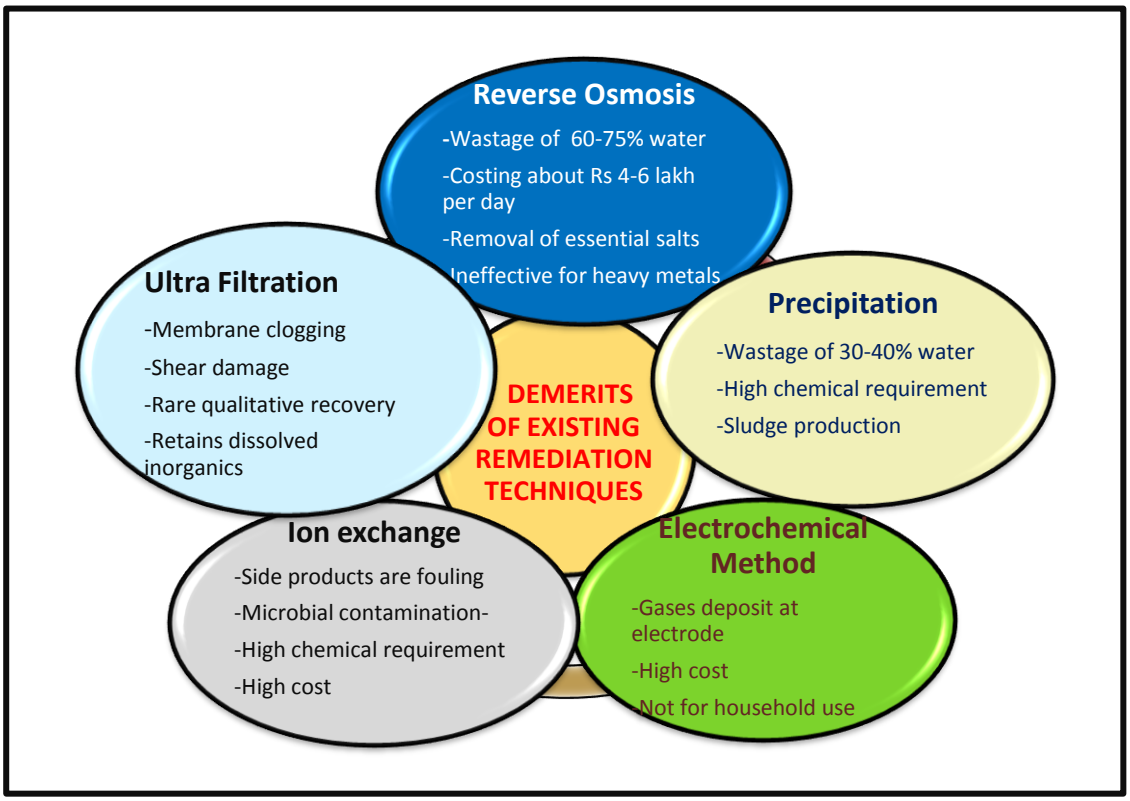
INTRODUCTION

Heavy Metals: Environmental Terrorists

Heavy metals, the important member of dirty dozen clubs of toxic pollutants are excessively released into various ecosystems of environment, making pollution of aquatic environment with toxic metals, a worldwide problem of major concern. Toxic metals like Cadmium, Chromium, Nickel, Lead, and Arsenic are released in industrial wastewaters and have well known toxic effects on flora and fauna. In view of high toxicity, environmental mobility and non-biodegradability of these metals, their removal from water has become absolute necessity. Traditional removal techniques include chemical precipitation, membrane filtration, reverse osmosis and ion exchange. Never the less, the application of such processes is restricted because of practical and economic constraints.

Existing Remediation Techniques: Demerits



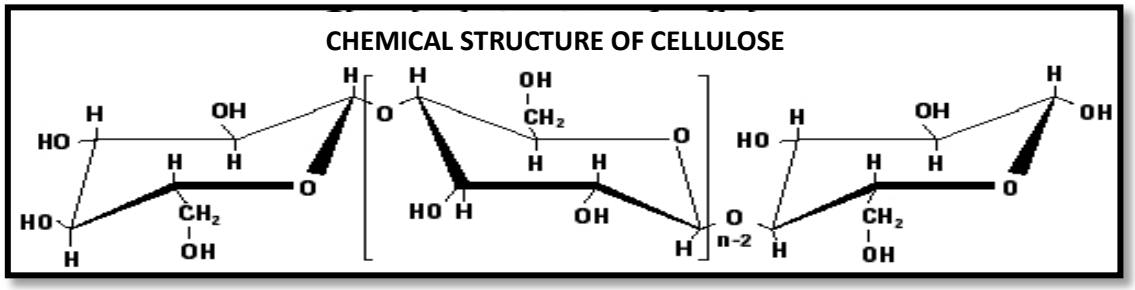
With increasing awareness on environment, the quest for cheap and cost effective technology for removal of heavy metals from industrial wastewaters has led to the use of low cost materials of plant origin as adsorbents. The search has brought newly emerging terms like ***environmentally benign chemistry***, ***safe chemistry, and sustainable chemistry*** or more popularly known as ***green chemistry*** to the foreground of scientific interest as a basis for designing of smart biomaterials for the use in developing water remediation technologies.

Biosorption: Emerging Trends of Remediation

Biosorption is an important phenomenon which is based on one of the twelve principles of green chemistry i.e. use of renewable resources. It is defined as the non-metabolically mediated passive binding of metals from water. Over the past years, intensive research on metal biosorption has established a solid base of knowledge, principles and highlighted enormous potential of this effective metal removal phenomenon for commercialization. The highest priority for commercialization of bioremediation is the assessment of cost of the raw material, stability, sorption efficacy, ability of product to meet out the technical requirements, practicability and competition with other techniques. In recent years, research interest has been focused on enhancement in the sorption efficacy and environmental stability of the biomass through environmentally safe chemical modifications, specifically aimed at increasing the density of effective functional groups responsible for sorption on biomass surface. Therefore, the selection of most economical and effective biomass is strategically important and their modifications/functionalization/charging of surface area become an area of sustained research.

Cellulose: Ideal biosorbent for surface modification

Biodegradable products from renewable materials are becoming increasingly more attractive due to escalating prices of synthetics. Recent research has focused on determining how to use biomass effectively as low cost, environment friendly raw materials in many products while reducing the dependence on petroleum based resources. Biomass, especially woody biomass, represents the most important sustainable resource which can be used as feedstock for producing bio products. Among biomaterials, recently, Cellulose has attracted the great scientific interest. Cellulose constitutes the most abundant renewable agricultural waste resource available worldwide and has plenty of advantages such as reasonable cost, biodegradability, availability, considerable stiffness, thermal recyclability and desired mechanical features. It was found that various functional groups present on their surface offer strong binding forces to the metal ions. The molecular structure of cellulose as a carbohydrate polymer comprises of repeating β-D glucopyranose units which are covalently linked through acetal functions between OH groups of C-4 and C-1 carbon atoms.

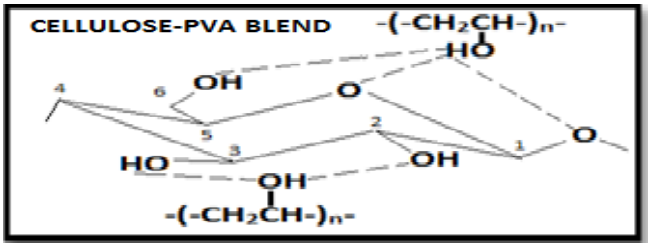


Unique characteristics of molecular structure of cellulose like large number of monosaccharide, three OH molecule per monomer unit, hydrophobic behavior due to presence of ester linked acetyl group and the presence of ether oxygen in the

glucopyranose ring monomer unit which is favorable for hydrogen bonding make it highly attractive for heavy metal ions scavenging applications particularly *(Pereira et al., 2009; Mota et al., 2013).* Cellulose has been regarded as an ideal reinforcing element for the preparation of eco composites because of its superb mechanical properties, excellent biodegradability and biocompatibility.

Cellulose-Polyvinyl alcohol Composites: Excellent High-Tech Biomaterial

Cellulose composites with polymers like polylactic acid, polycaprolactone, polyvinyl pyrrolidone, polyethylene glycol, polyhydroxy ethyl methacrylate, poly acrylamide and polyvinyl *alcohol (Yano and Nakahara, 2004; Azizi et al., 2005; Yuan and Ding, 2006; Kvien et al., 2007; Kvein and Oskman, 2007; Alemdar and Sain, 2008; Roohani et al., 2008; Yan and Gao, 2008; Fama et al., 2009)* as biodegradable matrices have started attracting attention with a view to altering their inherent properties *(Hepworth and Bruce, 2000; Formageau et al., 2003; Orts et al., 2005; Leitner et al., 2007; Das et al., 2010; Nigrawal et al., 2012; Mandal and Chakrabarty, 2014).* Among these polyvinyl alcohol is biological friendly synthetic polymer with properties such as water soluble, semi crystalline, fully biodegradable, non-toxic, excellent chemical resistance, good mechanical properties, high optical clarity, physical & chemical stability and biocompatibility, therefore, finds use in a broad spectrum of industrial applications *(Flaconneche et al., 2001; Wan et al., 2002; Hashim et al., 2005; Wan and Millon, 2007; Mohammadi et al., 2009; Chiciudean et al., 2011; Javadi et al., 2013)*. The combination of cellulose and polyvinyl alcohol has been found to possess excellent absorption properties, mechanical and thermal stability, processing capability and environmental biodegradability. The main functional uses of polyvinyl alcohol include filtration, catalysis, membranes, optics, drug release, enzyme mobilization, and tissue engineering, among others. On a molecular level, polyvinyl alcohol is layered structure with a double layer of molecules held together by strong Hydroxyl bonds, while weaker Vander Waal forces operate between the double layers. This folded chain structure leads to ordered regions (crystallites) within an unordered, amorphous polymer matrix. It is further attractive as it features a highly useful property of forming macro porous physically cross-linked composites. The basic properties of polyvinyl alcohol depend on the degree of polymerization, degree of hydrolysis, and tactility of macromolecular chains. In cellulose-polyvinyl alcohol blends the inter chain hydrogen bonds are formed mainly between the glucose ring ether oxygen and hydroxyl groups (OH) in polyvinyl alcohol while other bonds are also formed between secondary OH at either the C-2 or C-3 positions and the OH of the polyvinyl alcohol component. Such eco composites are supposed to exhibit remarkable properties, including ultralow density (4–500 kg m^{-3}), high porosity, high specific surface area, and excellent mechanical properties *(Tan et al., 2001; Pierre and Pajonk, 2002; Wu et al., 2012)*.



PRESENT STATE OF KNOWLEDGE

A detailed survey on the concerned topic has been carried out and presented precisely in the tabular fashion as follows:

Bio sorbents Used for Metal Removal: Table I

BIOSORBENTS	METALS REMOVED	REFERENCES
Waste fruit residues	Pb(II), Cd(II), Cu(II), Zn(II), Ni(II)	*Senthilkumar et al., 2000*
Crab shell	Cd(II), Zn(II), Ni(II), Cr(III & VI)	*An et al., 2001*
Marine algae	Pb(II), Zn(II), Cu(II)	*Qiming et al, 2001*
Petiolar felt-sheath of palm	Pb(II), Ni(II), Cd(II), Cr(III & VI), Zn(II)	*Iqbal et al., 2002*
Rice husk	Cd(II)	*Ajmal et al., 2003*
Olive mill residue	Cu(II), Cr (III)	*Veglio et al., 2003*
Wheat shell	Cu(II)	*Basci et al., 2004*
Agricultural waste	NI(II), Zn(II), Cd(II), Cr(II)	*Khan et al., 2004*
Sugar beet pulp	Cu(II)	*Aksu and Isoglu, 2005*
Egg shell	Cr(III), Cr(VI)	*Chojnacka K, 2005*
Sunflower stem	Cr(III), Cr(VI)	*Malik et al., 2005*
Husk of black gram	Cd(II), Cu(II), Ni(II), Zn(II)	*Saeed et al., 2005*
Papaya wood	Cu(II), Cd(II), Zn(II)	*Saeed et al., 2005*
Cellulose	Pb(II), Cr(III), Ni(II), Zn(II), Cd(II)	*Sungur and Babaoglu, 2005*
Coconut copra meal	Cd(II), Cr(III), Cr(VI)	*Ofomaja and Ho, 2006*
Crab shells	Cu(II), Co(II)	*Vijayaraghavan et al., 2006*
Tea waste	Cu(II),Pb(II)	*Amarasinghe and Williams, 2007*
Coconut shell carbon	Zn(II)	*Amuda et al., 2007*
Corncob	Pb(II), Cu(II)	*Jonglertjunya, 2007*
Modified Plant Wastes	Cd(II), Cu(II), Pb(II), Zn(II), Ni(II)	*Ngah and Hanafiah, 2008*
Tobacco stems	Pb(II)	*Li et al., 2008*
Coconut husk	Ni(II)	*Kehinde et al, 2009*
Zea mays	Pb(II), Cd(II), Ni(II),Cr (III), Cr(VI)	*Goyal and Srivastava, 2009*
Sugar beet pulp	Cu(II), Pb(II), Cd(II)	*Mata et al., 2009*
Groundnut hull	Pb(II)	*Qaiser et al., 2009*
Wheat based biosorbent	Cu(II), Zn(II), Cd(II), Pb(II), Ni(II)	*Farooq et al., 2010*
Waste tea and coffee	Cu(II), Zn(II), Cd(II), Pb(II)	*Djatiutomo and Hunter, 2010*
Rice & sun flower husk	Pb(II)	*Kafia and Shareef, 2011*
Red loess	Pb(II), Cu(II) and Zn(II)	*Xing et al., 2011*
Nano magnetic cellulose	Hg(II), Cu(II) and Ag (I)	*Donia et al., 2012*
Caladium bicolour	Pb(II) and Cr(III)	*Adefemi et al, 2013*
Bombax costatum calyx	Pb(II), Cd(III), Cr(II), Zn(II)	*Barminas et al., 2013*

Surface Modifications onto Polyvinyl alcohol Composites: Table II

COMPONENTS	MODIFICATIONS	REFERENCES
PVA & Starch	Poly(methacrylic acid)	*Beliakova et al., 2004*
PVA & Starch	Citric acid	*Shi et al., 2008*
PVA & Starch	Nano-SiO_2	*Tang et al., 2008*
PVA & Wood	Montmorillonite clay	*Jiang et al., 2011*
PVA & Cellulose	Polypropylene	*Cheng et al., 2007*
PVA & Cellulose	Alginic acid	*Cifci and Kaya, 2010*
PVA & Cellulose	Pentafluoropropyl methacrylate	*Hoebergen et al., 2003*
PVA & Cellulose	Phosphorous oxychloride	*Majmudar et al., 2005*
PVA & Cellulose	Tetramethylpiperidine oxy radical	*Mihranyan, 2013*
PVA & Methyl Cellulose	Cement	*Zhao et al., 2002*
PVA & Cellulose acetate	Alkali metal chloride	*Zhang and Qiu, 2003*
PVA & Cellulose acetate	Polyethylene glycol	*Muhammed et al., 2012*
PVA & Cellulose acetate	Polyethylene glycol	*Hassanien et al., 2013*
PVA & Cellulose Micro Fibril	Glyoxal	*Qiu and Netravali, 2012*
PVA & Cellulose Nano Fibril	Tetramethylpiperidine oxy radical	*Endo and Saito, 2013*
PVA & Cellulose Nanofibril	Silane-1 and Silane-2	*Javadi et al., 2013*
PVA & Cellulose Nanofibril	Montmorillonite clay	*Spoljaric et al., 2013*
PVA & Cellulose Nano Fibril	Multiwalled Carbon Nanotube	*Zheng et al., 2013*
PVA & Nanocellulose	Poly(acrylic acid)	*Pakzad et al., 2012*
PVA & Nanocellulose	d,l-lactide-co-glycolide	*Rescignano et al., 2014*
PVA & Me Carboxy Cellulose	Starch & Montmorillonite clay	*Taghizadeh & Sabouri, 2013*
PVA & Me Carboxy Cellulose	Starch & Montmorillonite clay	*Taghizadeh et al., 2013*

Modifications in the Properties of the Cellulose-PVA Composites: Table III

COMPONENTS	CHANGES IN THE PROPERTIES	REFERENCES
PVA & Cell Wall	Increase in Tensile Strength	*Bruce et al., 2005*
PVA & Cellulose	Increase in Young's Modulus	*Orts et al., 2005*
PVA & Cellulose	Increase in Young's Modulus	*Zimmermann et al., 2004*
PVA & Cellulose	Decrease in Intensity of OH^- Peak	*Majmudar and Adhikari, 2005*
PVA & Jute Nanofiber	Decrease in Melting Endotherm	*Das et al., 2010*
PVA & Nanocellulose	Increase in Thermal Stability	*Mandal and Chakrabarty, 2014*
PVA & Vegetable Tissue	Increase in Tensile Strength & Stiffness	*Hepworth and Bruce, 2000*
PVA & Bacterial Cellulose	Increase in Strain, Stiffness & Modulus	*Millon and Wan, 2006*
PVA & Bacterial Cellulose	Increase in Tensile Strength	*Gea et al., 2010*
PVA & Bacterial Cellulose	Increase in Tensile Strength	*Leitao et al., 2013*
PVA & Rice Straw Fibrils	Increase in Storage Modulus	*Wu et al., 2013*
PVA & Me cellulose	Decrease in Compressibility	*Kareem and Bermany, 2013*
PVA & Oxidized Cellulose	Increase in Solidity & Rigidity	*Mihranyan, 2013*
PVA & Me Carboxy cellulose	Decrease in velocity of Sound waves	*Formageau et al., 2003*
PVA & Me Carboxy Cellulose	Decrease in Density	*Kareem and Bermany, 2013*
PVA & Cellulose Microfibers	Increase in Tensile Strength & Stiffness	*Chakraborty et al., 2006*
PVA & Cellulose Micro Fibril	Increase in Glass Transition Temp.	*Qiu and Netravali, 2012*
PVA & Nano Cellulose	Increase in Thermal Properties	*Lee et al., 2009*
PVA & Cellulose Nanofibril	Increase in Tensile Strength	*Leitner et al., 2007*
PVA & Cellulose Nanofibrils	Increase in Elasticity & Porosity	*Zheng et al., 2013*
PVA & Cellulose Nano Fibers	Increase in Interfacial Compatibility	*Souza et al., 2010*
PVA & Cellulose Nano Fibers	Increase in Thermal Stability	*Frone et al., 2011*
PVA & Cellulose Nano Fibers	Increase in Tensile Strength	*Nigrawal et al., 2012*
PVA & Cellulose Nanocrystals	Increase in Viscosity & Conductivity	*Peresin et al., 2010*
PVA & Cellulose Nanocrystals	Increase in Tensile Strength & Modulus	*Zhang et al., 2012*
PVA & Cellulose Nanocrystals	Increase in Elongation Properties	*Rescignano et al., 2014*

Applications of Cellulose-Polyvinyl alcohol Composites: Table IV

COMPONENTS	APPLICATIONS	REFERENCES
PVA Hydrogel	Bioprosthetic Heart Valve	*Wan et al., 2002*
PVA Hydrogel	Wound Healing	*Bourke et al., 2003*
PVA Hydrogel	Plastic Packaging	*Lange and Wyser, 2003*
PVA & Cellulose	Double Layer Capacitor	*Hashim et al.,2005*
PVA & Cellulose	Taste Sensing Material	*Majmudar and Adhikari, 2005*
PVA & Cellulose	Metal Removal	*Cifci and Kaya, 2010*
PVA & Cellulose acetate	Ultrafiltration Membranes	*Zhang and Qio, 2003*
PVA & Cellulose acetate	Reverse Osmosis Membrane	*Muhammed et al., 2012*
PVA & Bacterial Cellulose	Soft Tissue Engineering	*Wan and Millon, 2005*
PVA & Bacterial Cellulose	Heart Tissue Replacement	*Millon et al., 2006*
PVA & Bacterial Cellulose	Soft Tissue Replacement	*Wan and Millon, 2007*
PVA & Bacterial Cellulose	Artificial Dura Mater for Brain	*Wang, 2007*
PVA & Bacterial Cellulose	Biomedical Applications	*Millon et al., 2008*
PVA & Bacterial Cellulose	Aortic Heart Valve Prosthesis	*Mohammadi et al., 2009*
PVA & Bacterial Cellulose	Artificial Cornea Biomaterial	*Wang et al., 2010*
PVA & Bacterial Cellulose	Aerospace Applications	*Chiciudean et al., 2011*
PVA & Cellulose Nanofibril	Organic Aerogels	*Javadi et al., 2013*
PVA & Cellulose Nanofibril	Barrier Films for Oxygen	*Spoljaric et al., 2013*
PVA & Cellulose Nanocrystals	Barrier Films for Oil	*Flaconneche et al., 2001*
PVA & Cellulose Nanocrystals	Tissue Regeneration	*Li et al., 2012*
PVA & Cellulose Nanocrystals	Biomedical Applications	*Kumar et al., 2013*
PVA & Cellulose Nanocrystals	Drug Delivery Strategies	*Rescignano et al., 2014*
PVA & Cellulose Nanocrystals	Super Absorbent for Oil	*Zheng et al., 2013*

HIGHLIGHTS OF THE LITERATURE SURVEY

The detailed survey of literature indicates:

- Abatement of toxic metals has been largely attempted using mainly inorganic and organic bio sorbents for cationic metal species and scanty information is available on the ability of biomaterials to remove anionic metal species.

- Finally, none of the methods using inorganic and organic biomass has reached to the commercial level.

- No attention seems to be paid to use wood pulp as such (largely cellulosic material) and its modification for the abatement of toxic metals.

- Cellulose-polyvinyl alcohol composites have been established for excellent mechanical, thermal stability, processing capabilities and environmental biodegradability and are largely explored for various applications like catalysts, membranes, optics, drug release, enzyme mobilization, tissue engineering and biomedical applications.

- However, not much research attention has been paid to exploit cellulose-polyvinyl alcohol unexplored potential as heavy metal scavenger from water bodies.

OBJECTIVES

The present work aims towards the synthesis, functionalization and characterization of target specific wood pulp-polyvinyl alcohol composites with enhanced sorption efficiency and environmental stability for a simple, eco friendly, cost effective pretreatment step before large scale chemical treatments for the removal of cationic and anionic species from water bodies.

PLAN OF WORK

1. **Synthesis of Wood pulp-Polyvinyl alcohol composite-**

- *Polymerization of wood pulp with polyvinyl alcohol for surface enrichment of functional groups (OH).*

2. **Functionalization on Wood pulp-Polyvinyl alcohol composite for the sorption of cationic metal species-**

- *Esterification with saturated poly carboxylic acids (Succinic and Citric acid).*
- *Co-polymerization with Acrylic and Itaconic acid on wood pulp-polyvinyl alcohol composite.*

- *Chelation by nitrogen containing chelating agents–(2-picolylamine and 2-aminopyridine) on wood pulp.*

3. **Functionalization on Wood pulp for the sorption of anionic metal species-**

- *Polymer grafting with Glycidyl Methacrylate.*
- *Polymer grafting with N, N′-methylene bisacrylamide.*

4. Characterization of native Wood pulp-Polyvinyl alcohol composite, surface modified Wood pulp-Polyvinyl alcohol composite and functionalized Wood pulp by following standard methods-

- *Scanning Electron Microscopy*
- *Thermo Gravimetric Analysis*
- *Atomic Force Microscopy*
- *FTIR Spectroscopy*
- *X-ray Diffraction*
- *Zeta Potential*

5. Optimization of standard conditions for maximum sorption of cationic and anionic metal species onto developed smart biomaterial-

- *Batch experiments as a function of pH, biosorption dose, concentration of metal species, contact time and initial volume of laboratory prepared and real water samples.*

6. Reusability of metal loaded Wood pulp-Polyvinyl alcohol composite/ functionalized Wood pulp-Polyvinyl alcohol composite-

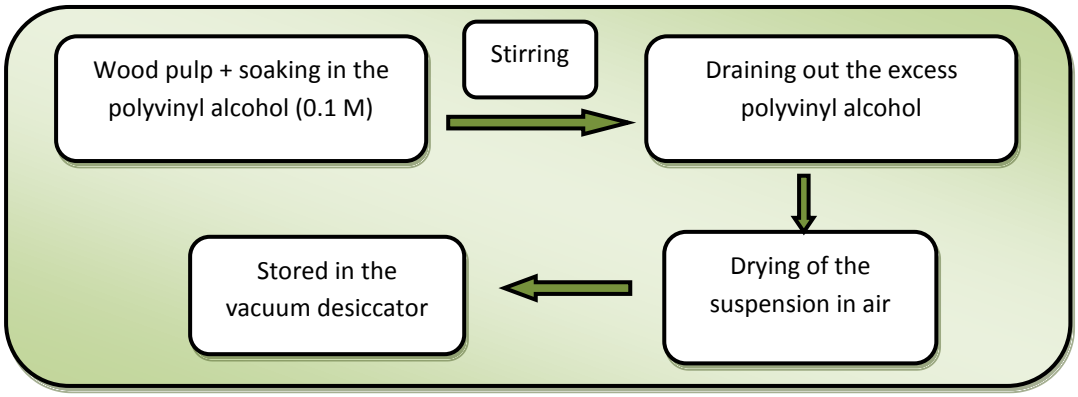
In order to design the proposed method of decontamination of metals, more economical, series of sorption and desorption batch experiments would be conducted by eluting the biomass with following acids:

- *Mineral acids*
- *Organic acids*

METHODS AND METHODOLOGY

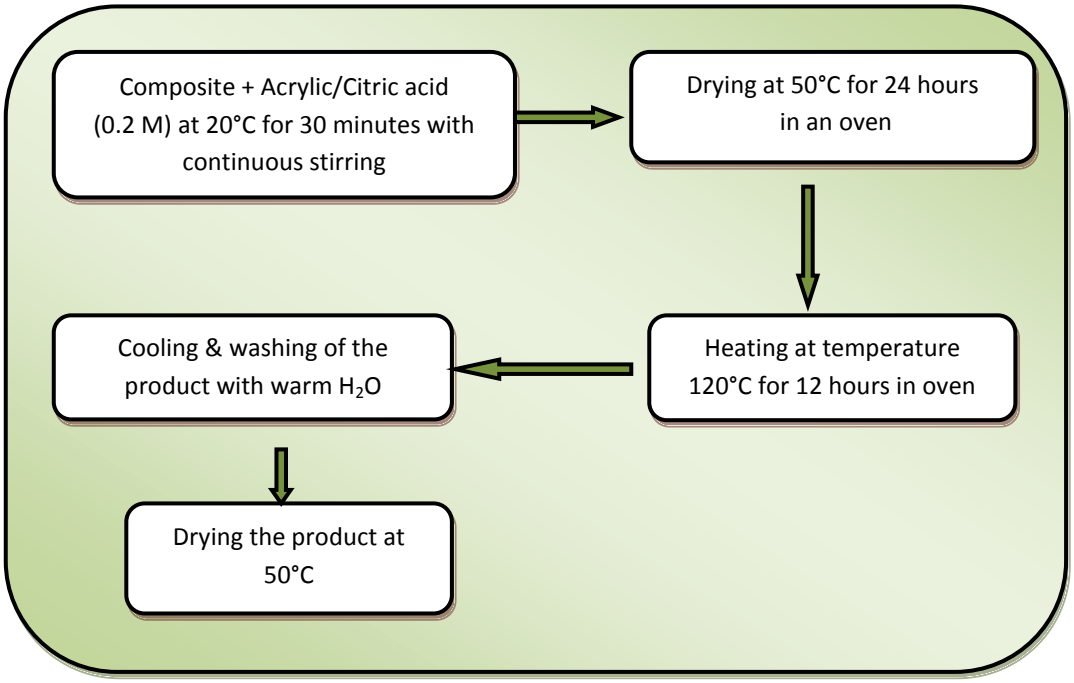
Experimental details are depicted schematically as follows:

1. ***Synthesis of Wood pulp-Polyvinyl alcohol composite:***

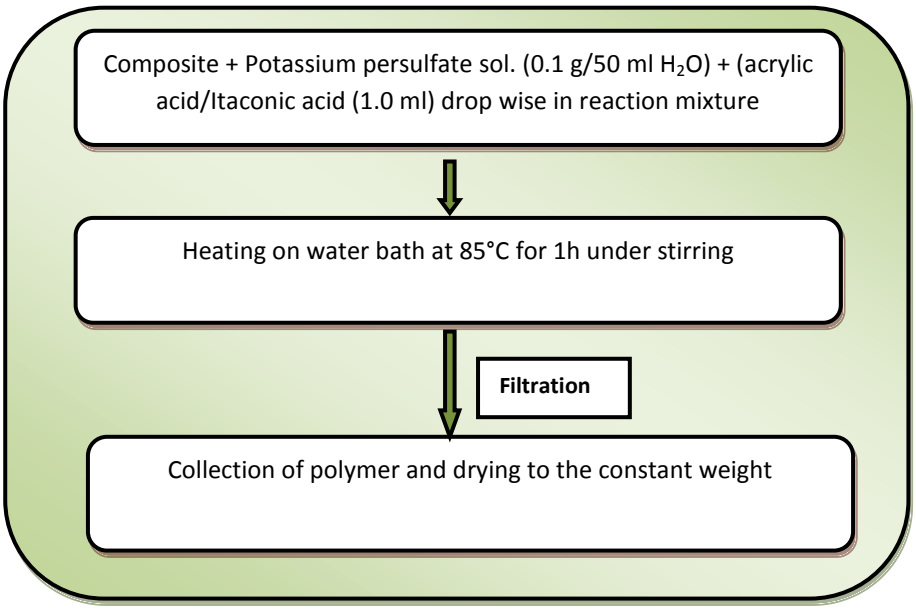

Wood pulp + soaking in the polyvinyl alcohol (0.1 M)
Stirring
Draining out the excess polyvinyl alcohol
Drying of the suspension in air
Stored in the vacuum desiccator

2. ***Functionalization on composite for the sorption of cationic metal species.***

- ***Esterification:***

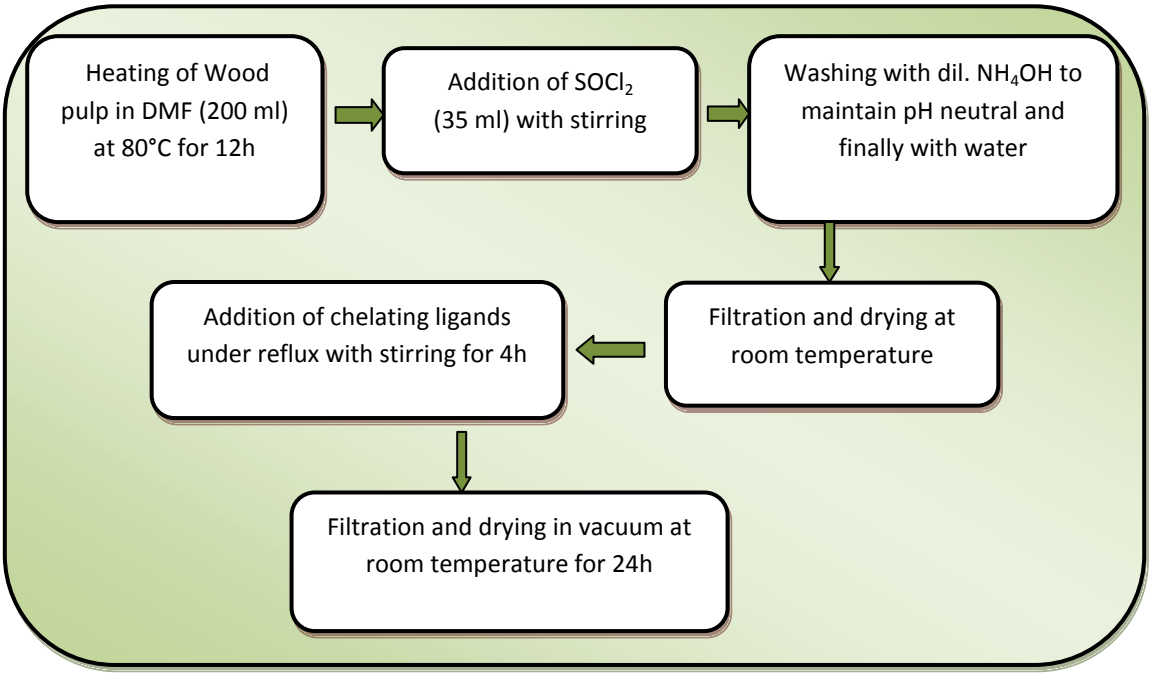

Composite + Acrylic/Citric acid (0.2 M) at 20°C for 30 minutes with continuous stirring
Drying at 50°C for 24 hours in an oven
Heating at temperature 120°C for 12 hours in oven
Cooling & washing of the product with warm H_2O
Drying the product at 50°C

- ***Graft Co-polymerization:***


Composite + Potassium persulfate sol. (0.1 g/50 ml H_2O) + (acrylic acid/Itaconic acid (1.0 ml) drop wise in reaction mixture
Heating on water bath at 85°C for 1h under stirring
Filtration
Collection of polymer and drying to the constant weight

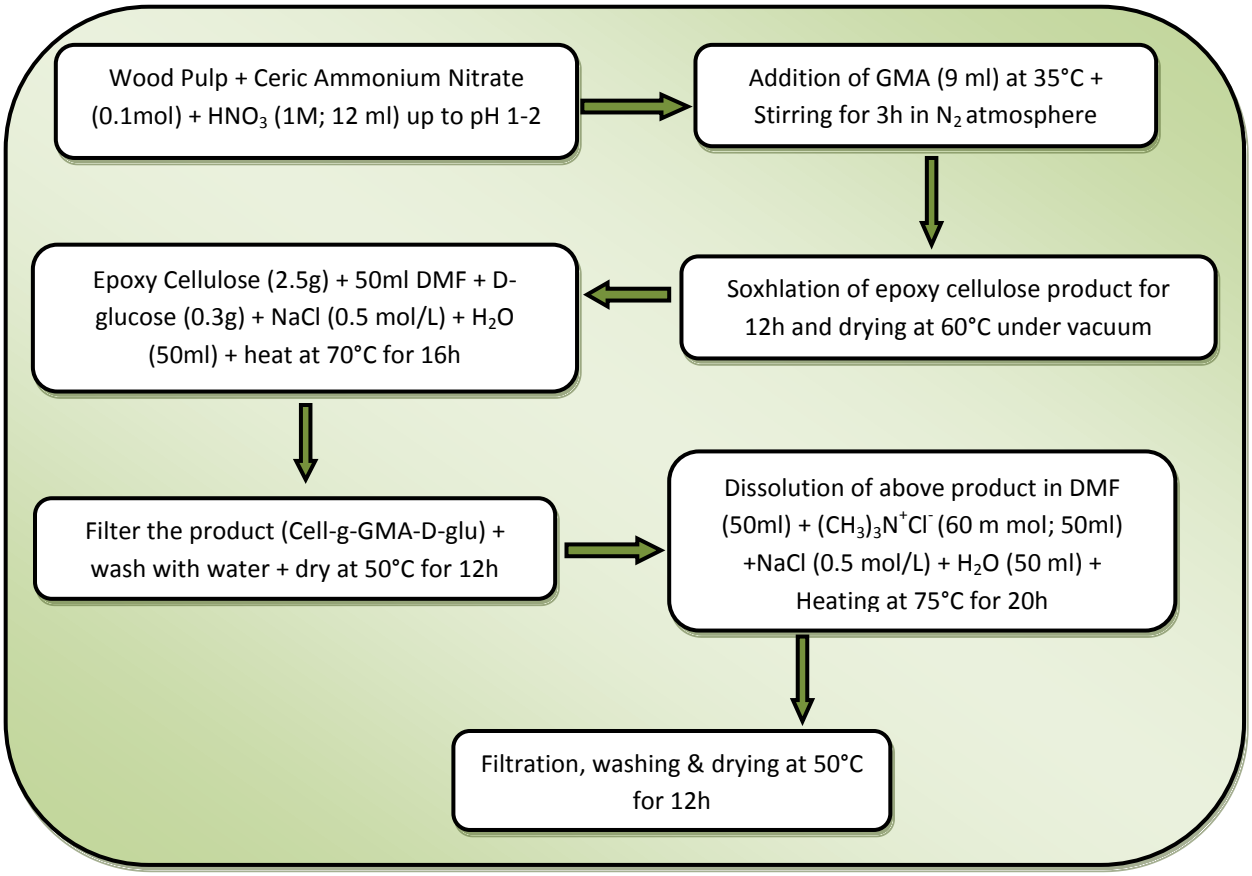
3. *Functionalization on Wood pulp for the sorption of cationic metal species*

- ***Chelation:***

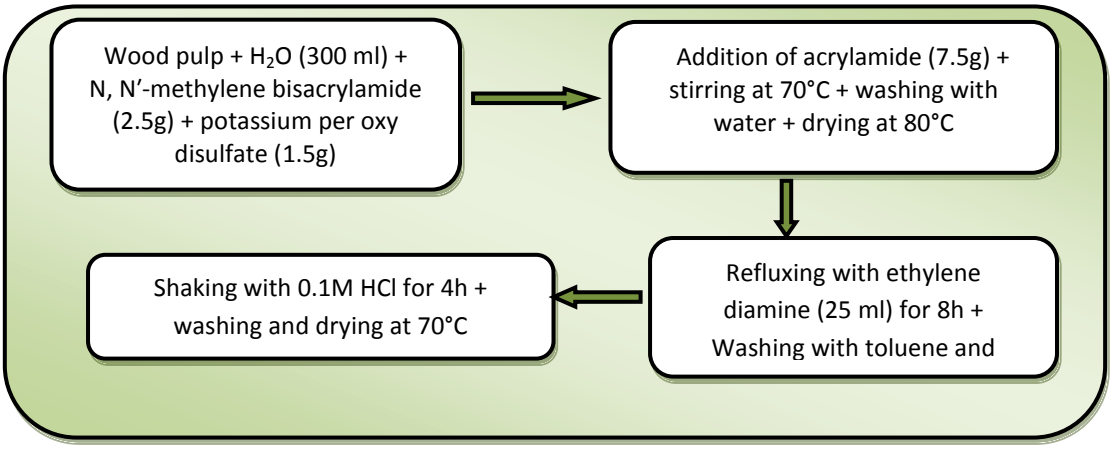

Heating of Wood pulp in DMF (200 ml) at 80°C for 12h
Addition of $SOCl_2$ (35 ml) with stirring
Washing with dil. NH_4OH to maintain pH neutral and finally with water
Filtration and drying at room temperature
Addition of chelating ligands under reflux with stirring for 4h
Filtration and drying in vacuum at room temperature for 24h

4. *Functionalization on Wood pulp for the sorption of anionic metal species.*

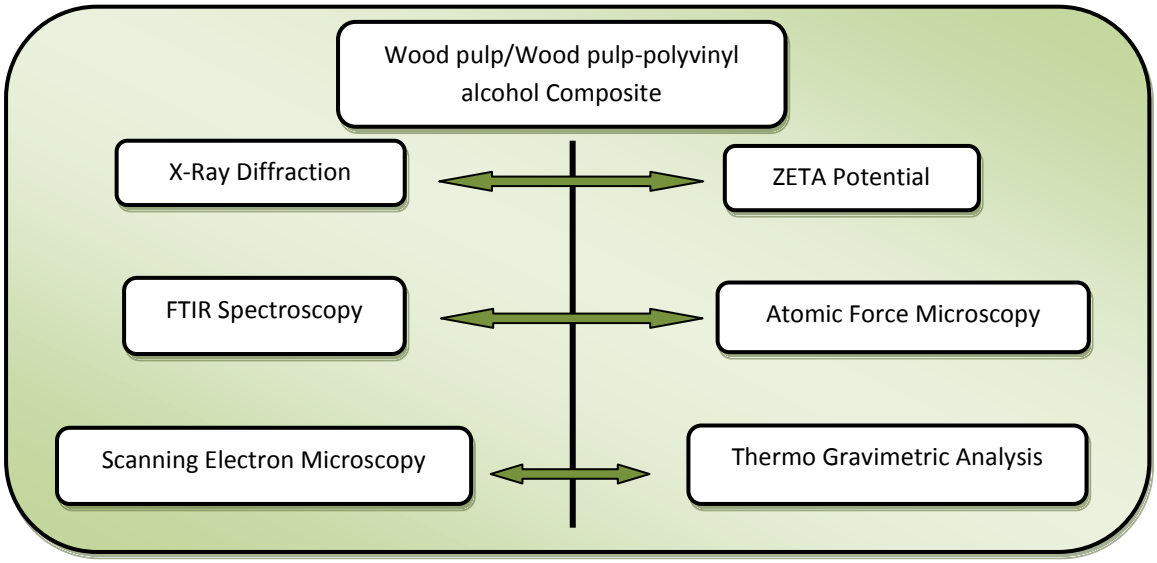
- ***Glycidyl Methacrylate (GMA):***


Wood Pulp + Ceric Ammonium Nitrate (0.1mol) + HNO_3 (1M; 12 ml) up to pH 1-2
Addition of GMA (9 ml) at 35°C + Stirring for 3h in N_2 atmosphere
Soxhlation of epoxy cellulose product for 12h and drying at 60°C under vacuum
Epoxy Cellulose (2.5g) + 50ml DMF + D-glucose (0.3g) + NaCl (0.5 mol/L) + H_2O (50ml) + heat at 70°C for 16h
Filter the product (Cell-g-GMA-D-glu) + wash with water + dry at 50°C for 12h
Dissolution of above product in DMF (50ml) + $(CH_3)_3N^+Cl^-$ (60 m mol; 50ml) +NaCl (0.5 mol/L) + H_2O (50 ml) + Heating at 75°C for 20h
Filtration, washing & drying at 50°C for 12h

- ***N,N´-methylene bisacrylamide:***

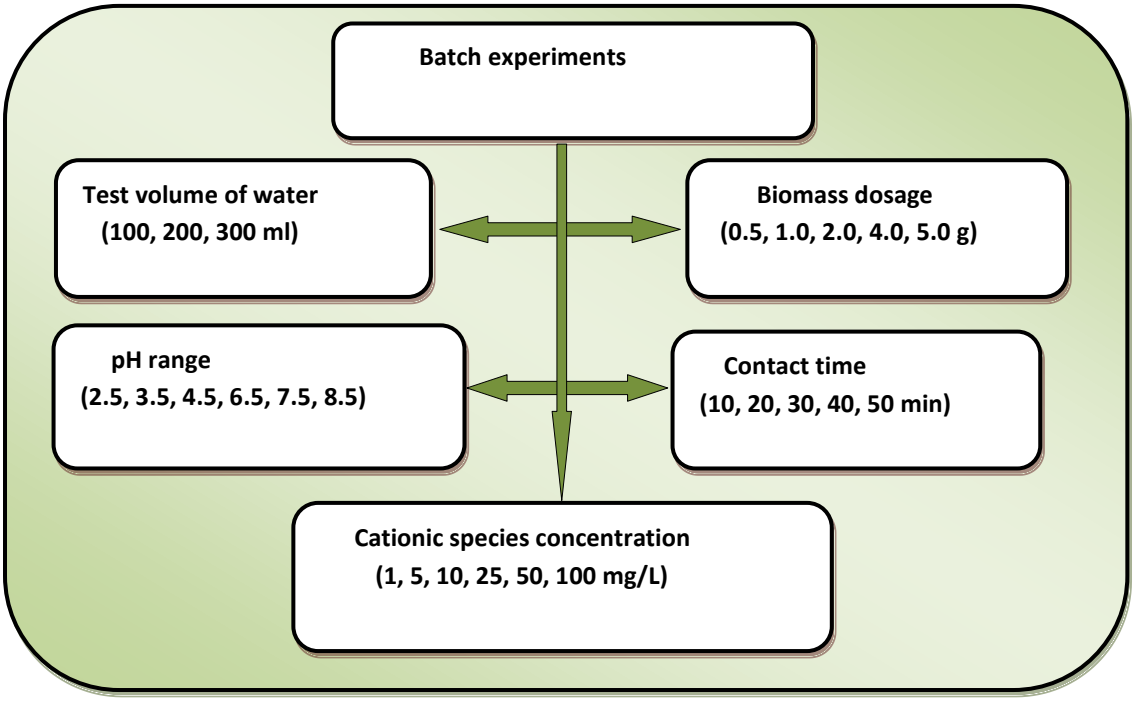

Wood pulp + H_2O (300 ml) + N, N'-methylene bisacrylamide (2.5g) + potassium per oxy disulfate (1.5g)
Addition of acrylamide (7.5g) + stirring at 70°C + washing with water + drying at 80°C
Refluxing with ethylene diamine (25 ml) for 8h + Washing with toluene and
Shaking with 0.1M HCl for 4h + washing and drying at 70°C

5. *Characterization methods:*

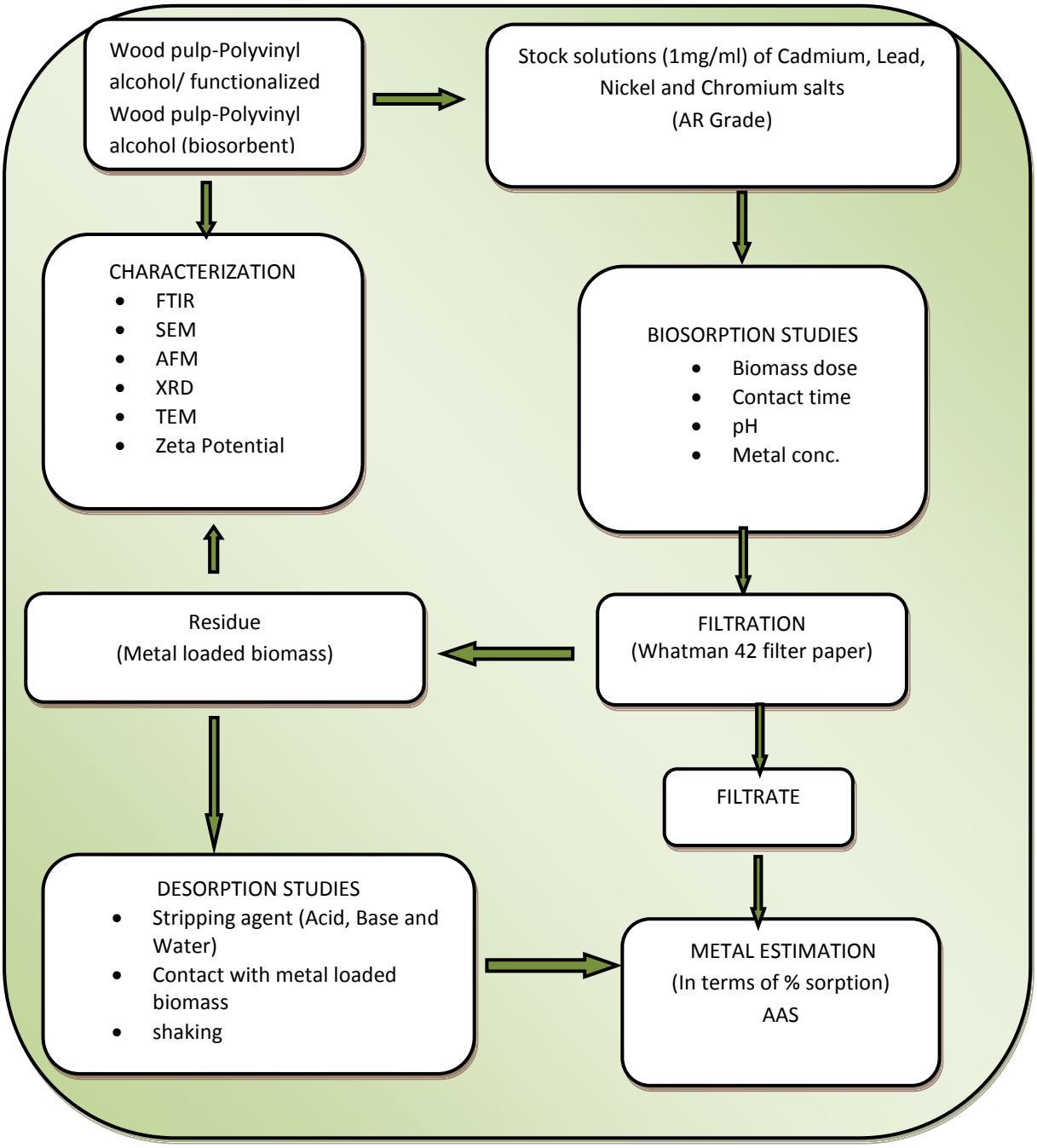


6. *Experimental conditions for sorption:*

Sorption efficiency at laboratory scale using standard practices would be carried out in batch Experiments under various experimental conditions-


Batch experiments
Test volume of water (100, 200, 300 ml)
Biomass dosage (0.5, 1.0, 2.0, 4.0, 5.0 g)
pH range (2.5, 3.5, 4.5, 6.5, 7.5, 8.5)
Contact time (10, 20, 30, 40, 50 min)
Cationic species concentration (1, 5, 10, 25, 50, 100 mg/L)

7. ***Standardization of Wood pulp-Polyvinyl alcohol/Functionalized Wood pulp-Polyvinyl alcohol Composite for the evaluation of metal sorption and regeneration of bio mass:***



SIGNIFICANCE OF THE WORK

Modified Wood Pulp- PVA composite with enhanced sorption potential, environmental stability and recyclability would have potential to be used as sorbent for the development of low cost, domestic and eco friendly method for remediation of cationic and anionic metal species from water bodies for rural and remote areas of the country.

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